INFRARED ABSORPTION OF HYDROGEN IN NITROGEN COMPOUNDS; THE EFFECT OF HYDROGEN BONDING ON THE CARBONYL ABSORPTION

BY

GRAHAM WATSON McMILLAN

B.S., Monmouth College, 1937

AN ABSTRACT OF A THESIS

SUBMITTED IN PARTIAL FULFILLMENT OF THE REQUIREMENTS
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INTRODUCTION

Since the formulation of the theory of hydrogen bonding, a body of literature on the subject has arisen.[1-5] Interest has been focused primarily on the contribution of the bond to the physical behavior of the molecules involved. However, in addition, peculiar chemical behavior, concerning such properties as acidity and basicity, as well as chemical reactivity, may often be resolved by a proper reference to the theory.[6-8] But perhaps the most fruitful application may yet lie in the field of physiological structure. Certain work undertaken in this laboratory indicate that the bond is specifically concerned in the function of carbohydrates and proteins.[9-11]

The use of infrared light in studying the vibrations of hydrogen atoms in the region of 3μ has furnished the best single approach to the problem. Under such circumstances it is valid to assume that the molecular motions studied are discrete from, and unaffected by, other vibrations of lower frequency. Such studies furnish data on the hydrogen bond which are uncomplicated by the intrusion of the effects of other types of molecular interaction. But the lower frequency vibrations of other molecular groups can not be studied with the same simplicity. For a great deal more uncertainty should be attached to attempts to identify low frequency oscillators with certain vibrational bands; since, in these cases, vibrations are much more sensible to other motions in the molecule. So until recently studies of hydrogen bonding by means of infrared spectroscopy have been confined almost entirely to absorptions in the region of the hydrogen valency motions.

It is well-known that molecules containing carbonyl groups have an absorption in the neighborhood of 6μ. This absorption is believed to be due to a vibration which occurs principally in the direction of the valence.

Lecomte[12] found that the aldehyde frequency was slightly higher than that for the ketone. He also established that aromatic carbonyls vibrate with a lower frequency than do aliphatic. From the several studies on carboxylic acids,[13-17] it seems definite that in this instance the group has two vibrations associated with it. One of these is peculiar to the group in the dimer structure; the other is due apparently to the unperturbed group. Raman data has substantiated this view. Several authors have concluded[18-20] that the two Raman shifts observed for the fatty acid carbonyl are caused by the group in the dimer, on the one hand, and by the monomeric structure on the other.

The formation of hydrogen bonds in this case, then, has an effect on the carbonyl vibration. But a precise knowledge of the effect of bonds of medium strength on the carbonyl group is lacking. Nor has it been established that other types of molecular interaction do not, also, alter the vibrational spectrum of the group.

An evaluation of the effect waits on studies of the absorption spectra under widely different circumstances of structure.

EXPERIMENTAL

The spectroscope used in these studies contained a grating of the echellette type. It was ruled 3600 lines to the inch on a block of tin having a face 10x15 centimeters, at the University of Michigan. The flame angle of the echellette was about 25°. These conditions led to a maximum efficiency in the neighborhood of 6μ. Intermediate between the grating and the Nernst glower, which acted as source, was located a halite prism sputtered with silver. This arrangement was used to insure that only one order would be focused eventually on the thermocouple. A complete description has been given by Sleator.[21]

The impulses from the spectroscope thermocouple were amplified by a Moll relay which has been described fully by its manufacturers, P. J. Kipp & Zonen, Delft.

EXPERIMENTAL RESULTS AND DISCUSSION

Previous work from this laboratory[22-23] on the absorption spectra of acid amides in the region of the hydrogen valence absorptions has pointed to the existence of two types of molecular aggregates. While both involve N-H-O bonds, one structure is a linear polymer and the other is a ring dimer.

The present work substantiates the conclusion that only N-H-O bonds occur; and demonstrates the absence of any appreciable amount of enolization.

Evidence obtained in these studies indicates a mode of vibration, ν_4,[26] for the carbonyl group, in which the oxygen atom at any instant is moving in a direction opposite to that of the rest of the molecule. An alternate mode of vibration, ν_2, postulated in the case of formaldehyde,[27] consists essentially in a bending frequency of the hydrogen atoms.

It is suggested that substitution of other and heavier radicals in place of the hydrogen atoms would reveal a sensitive relationship between mass and frequency of vibration, if the normal mode

were a bending frequency. This is not the case. It can only be concluded that ν_2 is an incorrect assignment and that ν_4 is a more logical picture of the vibration.

In the course of the investigation it was necessary to determine the utility of this technique and to estimate the various factors which, in addition to hydrogen bonding, might modify or distort the vibration of the carbonyl group. So, before a precise answer could be made as to the effect of bonding on the group, the behavior of the carbonyl had to be determined for molecules in which no such interaction could occur. For this reason ketones and esters were studied. Then, in order to discover the character of the carbonyl in amides themselves, N, N-dimethylacetamide was investigated, since it was supposed that its absorption spectrum, likewise, would be uncomplicated by the chance of strong molecular interactions.

In each of these instances common properties of the group were observed. Without exception, the absorption was intense, as would be expected for a fundamental vibration of the parallel type. Furthermore, in each case the band was split into two maxima. The possibility of this splitting being due to accidental degeneracy was discounted because of the wide variety of structures in which the effect was displayed. These separations are of the order of 0.025μ which differs by a factor of 6, or more, from the separations recorded by other investigators for the distance between normal carbonyl absorption and that due to the hydrogen-bond perturbed group. Table I lists the location of the two maxima and the degree of their separation for the carbonyl group in several molecules.

TABLE I

Solutions in CCl_4	Wavelength (μ)		Separation (μ)
Acetone	5.808	5.830	0.022
Benzophenone	5.978	6.006	0.028
Cyclopentanone	5.688	5.708	0.020
Ethyl acetate	5.712	5.740	0.028
Diethyl carbonate	5.706	5.734	0.028
N, N-dimethylacetamide	6.005	6.061	0.036
N-methylacetamide	5.908	5.964	0.036
N-cyclohexylacetamide	5.922	5.968	0.046

Comparisons of data obtained on solutions of these molecules with those obtained on the molecules in the vapor or liquid states pointed to several generalizations.

It was found that the difference in location between the center of absorption for acetone vapor and acetone solution and, again, for ethyl acetate and its solution, amounted to about 0.07 μ which corresponds closely to the difference in absorption of HCl vapor and solution, as determined previously in this laboratory. This might indicate that difference in absorption observed between the vapor state and dispersion in an inert solvent are provoked by some factor peculiar to the solvent.

From the great similarity between absorptions of solutions and those of the pure condensed phase of the solute, it was concluded that, in the case of solutes of low dipole moment or of those which can attain a maximum degree of association in solution, a sort of external pressure modifies the normal vibrations of the molecule.

But carbonyl spectra do not always display this close correspondence. Superimposed on its normal behavior, in certain cases, there appears an effect which is a function of concentration and which is observed in the infrared spectrum as a shift in the center of absorption toward longer wavelengths as the concentration is increased. In fact, inspection of the absorption band as it changes leads to the conclusion that the effect increases toward a limit set by the pure material. This occurs wholly apart from hydrogen bond formation as it is ordinarily defined. It is present to a much greater extent in ketones than in esters. The absorption of esters is amazingly constant from solution to liquid. But N, N-dimethylacetamide absorption begins to deviate at still a lower concentration, indicating that the interaction is still stronger in this instance.

Solutions of cyclopentanone in mixtures of CCl_4 and $CHCl_3$ show that the change of absorption with concentration and that due to the formation of the hydrogen bond may be competitive effects. It is noticed that the percentage change of absorption upon increasing the concentration of $CHCl_3$ in a dilute solution of the ketone is greater than in the case of similar treatment of a more concentrated solution. In other words, the cause of the shift in absorption which occurs as the concentration of the ketone is increased tends to inhibit further shifts which occur as hydrogen bonds are formed. It is known that $CHCl_3$ forms only weak bonds with ketones.[24] Furthermore it is supposed that CCl_4 forms polarization complexes with the carbonyl linkage. Müller[25] suggests loose complexes to account for the abnormal polarization of acetone in CCl_4. And the peculiar heat of mixing of N, N-dimethylacetamide is well-known. If the formation of the polarization complex were dependent on the polarization of the carbonyl linkage by the close

approach of neighboring dipoles, then above a certain minimum concentration complex formation would be a function of concentration. In addition, it is apparent that the formation of such a complex would tend to inhibit the formation of hydrogen bonds with the $CHCl_3$ in the mixture.

Another possible explanation lies in the fact that the frequency of vibration may change as the dielectric of the medium changes. It is recognized that the degree of polarization of a dipole is a function of the close approach of other dipoles. Where this occurs to alter the direction of the moment associated with a given oscillator, a change in the anharmonicity should result. And the change in energy terms should be reflected in the vibrational spectrum.

Data were obtained on the first harmonic of the carbonyl vibration. Cyclopentanone solutions of high concentration were run in this region with the product of cell-length and concentration kept constant. Thus if any change in the absorption of the harmonic transition had occurred it would have been measured in quantitative fashion. Such slight differences as did appear are believed to lie within the experimental error so that significance is not attached to them.

In an effort to discover the relationships of the anharmonicities of these molecules various ketones and esters, as well as N, N-dimethylacetamide were run in the region of 3 μ and their anharmonicity coefficients, a, were calculated by means of the expression for the anharmonic oscillator.

$$W = (n+\tfrac{1}{2})h\nu_0 - a(n+\tfrac{1}{2})^2 h\nu_0$$

The values of the anharmonicity coefficients are listed in Table II.

TABLE II

Solutions in CCl_4	$a \times 10^3$
Acetone	6.9
Ethyl acetate	8.0
Benzophenone	5.4
Diethylcarbonate	1.7
Cyclopentanone	8.0
N, N-dimethylacetamide	68.0

Over the concentration range in which the hydrogen bond first begins to be detected by spectroscopic means in a mono-substituted aliphatic amide, an abnormal absorption of the carbonyl group was observed. The abnormality consisted in a shift of the center of absorption toward longer wavelengths. This was interpreted as indicating that the principal effect of the hydrogen bond on the

carbonyl group was a lengthening of the carbon-oxygen valence. It was supposed that if bonding occurred to the adjacent nitrogen atom, the coincident increase in the potential gradient along the direction of the carbonyl valence would demand a shift to higher frequencies rather than lower ones.

If tautomerism were occurring to any extent in the amides the absorption coefficient of molecules would be different from those for similar molecules in which there was no chance of two tautomers. This is not the case. The absorption coefficients for N, N-dimethylacetamide, N-methylacetamide and N-cyclohexylacetamide are all very nearly equal to 200.

The advantage in employing infrared spectra as a means of detecting hydrogen bonds rests primarily on the fact that in the region of hydrogen frequencies other types of interactions do not influence the result. The vibration of the carbonyl group which occurs with a much lower frequency reflects other types of interaction as well as the formation of the hydrogen bond. And it is entirely possible that interactions of one kind or another occurring at portions of the molecule remote from the carbonyl group would be reflected in an altered motion of that group.

However, a study of lower frequency vibrations should yield evidence as to the characteristics and behavior of other types of interaction. It is probable that the region between 6μ and 15μ would prove fruitful in this respect.

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VITA

Graham Watson McMillan was born in Monmouth, Illinois, on September 25, 1916. He attended public schools in Monmouth. From 1929 to 1933 he attended Monmouth High School. The next four years, 1933-1937, he was enrolled in Monmouth College, receiving the Bachelor of Science in June, 1937. The same year he entered the graduate school of the University of Illinois as a University Scholar. Since September, 1938, he has held a special research assistantship in physical chemistry made possible through the Rockefeller Foundation. He is a member of Gamma Alpha, Phi Lambda Upsilon and Sigma Xi. He is co-author of three papers, "Infrared Absorption of Phenylmethane," J. Am. Chem. Soc., **61,** 1053 (1939) and "Infrared Absorption Studies of Some Hydrocarbons," J. Am. Chem. Soc., **62,** 2225 (1940) with Dr. F. T. Wall, and "Infrared Absorption Studies VIII. Hydrazoic Acid," J. Am. Chem. Soc., **61,** 2809 (1939) with Drs. A. M. Buswell, W. H. Rodebush and F. T. Wall.